Effect of Phosphate Salts on the Thickening and Gelation of Some Concentrated Milks

Milk concentrates which have not been exposed to a drastic heat treatment during processing undergo progressive thickening and an irreversible gelation in storage. This applies not only to concentrates preserved by high temperature-short time (HTST) sterilization, but also to concentrates preserved by freezing, and to those preserved by means of high concentrations of sugar. Such milks will be referred to as low heat concentrates.

The thickening which is observed during the storage of milk concentrates is essentially a coagulation phenomenon, and it is pertinent to inquire whether these coagulation processes have a common mechanism. The thickening appears to be related because the orthophosphates which stabilize evaporated milk toward heat coagulation (1) fail to exhibit a similar function in stabilizing the three types of low heat concentrates during storage (2, 3, 4).

The negative results obtained with the orthophosphates constitute evidence of a kind in support of a common mechanism but they are inconclusive and without practical value. More positive and practical results would be at hand if a compound could be found which would stabilize all low heat milk concentrates against age thickening and gelation. Extensive studies on the use of polyphosphates as stabilizers in HTST sterilized milk concentrates have established the utility of these compounds in retarding gelation (5). It appeared likely that the polyphosphates would also be effective in stabilizing both frozen milk and sweetened milk concentrates. Experiments were undertaken to test this view, and it is the purpose of this paper to present and to discuss the results of these experiments.

Of a number of polyphosphates available for study, the polyphosphate glass known as sodium tetraphosphate was found to be quite effective and most of the experiments were carried out with this substance.

Following the completion of our studies a very recent dissertation by Wallgren became available describing experiments in which the tetraphosphate was employed successfully in frozen milk (6). Reference was made to the work of Doan and Warren who earlier had achieved the same success (3). The results obtained by these investigators will be discussed.

EXPERIMENTAL

Materials

The polyphosphates were either commercial products or were made in the laboratory by the fusion of mixtures of monobasic and dibasic sodium phosphate. The tetrapolyphosphate glass which was used predominantly was a commercial product in which the average number of phosphorus atoms was 4.8 per chain.

Milk was obtained from the U.S. Department of Agriculture herd.

Equipment

A Mallory[1]) coiled tube heat exchanger was available for either forewarming or sterilization and subsequent cooling. Homogenization following sterilization was carried out in a Manton-Gaulin high pressure homogenizer. Concentration was effected in a Rogers vacuum pan assembly equipped with steam jets and a condensate pump to maintain a high vacuum (28 inches) during evaporation. In the preparation of sterile products aseptic packaging facilities were available. Samples were stored in 6 ounce cans. In the preparation of sweetened condensed milk a 5 gallon size candy kettle was employed to achieve adequate cooling and agitation during lactose crystallization.

Methods of Measurement

Viscosity measurements were made on the sterile and thawed frozen milks at 30°C with a transpiration type viscometer operating at a maximum shearing stress of 175 dynes/cm^2. Thawing of the frozen milk was conducted at 4.4°C for 24 hours. The melted samples were stirred and equilibrated 1 hr. at 30°C prior to measurement. The storage life of the sterile milk concentrates was considered to end when the viscosity during storage increased to a value equal to twice the minimum value observed during storage. The storage life of the frozen milk concentrates was considered to end when in the reconstituted milks more than 2% sediment was present. Analysis for sediment was conducted as follows: The frozen milk was thawed at 4.4° for 24 hrs. Twenty-five gram samples at 4.4° were mixed with sufficient cold water at that temperature to yield milks containing 12.6% solids. The mixture was swirled to achieve intimate mixing, held 24 hrs. at 4.4°, swirled again, and then introduced into 10 ml. graduated centrifuge tubes. After the tube contents at 4.4° had been centrifuged in an International Centrifuge, Size 2, Model V, for 5 minutes at 222$\times$G (1000 r.p.m.), the quantity of sediment was measured by referring to the graduations on the centrifuge tubes.

Body changes in sweetened condensed milk were followed with a Brookfield viscometer.

[1]) The use of trade names is for the purpose of identification only, and does not imply endorsement of the product or its manufacturer by the U.S. Department of Agriculture.

RESULTS

Sterile Milk Concentrates

Fresh milk was standardized to a fat to nonfat solids ratio of 1:2.25, forewarmed at 138° for 15 seconds, concentrated to about 37.6% solids, and standardized with water or additive solution to contain 36% solids and 0.05% sodium tetraphosphate or orthophosphate buffer salts based on the weight of the original milk (12.6% solids). The 36% concentrate was sterilized at 138°C for 15 seconds, cooled to 71°C, aseptically homogenized at 7500–500 p.s.i., cooled to 20° and canned aseptically. Results of viscosity measurements are tabulated in Table 1.

TABLE 1

Effect of Addition of Sodium Ortho- and Tetrapolyphosphate on Thickening and Gel Formation in High Temperature-Short Time Sterilized Milk

Storage Time	*Storage Temperature*	*Viscosity at 30°C*		
		No Additive	*Orthophosphate*	*Tetrapolyphosphate*
days	°C	cp.	cp.	cp.
0		31	19	15
20	20	41	58	15
	30	47	62	14
	37	48	113	16
40	20	66	137	16
	30	92	gel	15
	37	gel	gel	19
100	20	115	gel	17
	30	gel	gel	18
	37	gel	gel	33
180	20	gel	gel	18
	30	gel	gel	24
	37	gel	gel	79
Storage Life		*days*	*days*	*days*
	20	45	16	>180
	30	30	13	>180
	37	26	10	84

Additive usage was 0.05% based on the weight of 12.6%TS milk.
Solids content of milk, 36%.
Viscosity measurements made at maximum shearing stress of 175 dynes/sq. cm.
Storage life calculated as time in days for viscosity to reach a value equal to twice the viscosity of the freshly stored milks.

A profound increase in storage life was brought about with the use of the polyphosphate, whereas a significant decrease attended the use of the orthophosphate mixture. At 30°C for example, storage lives of the control concentrate, the orthophosphate containing concentrate, and the polyphosphate containing concentrate were 30, 13 and more than 180 days, respectively.

A number of experiments on sterile concentrates were carried out, the results of which have not been recorded here. An experiment in which the polyphosphate concentration was varied showed a marked initial thickening effect of the poly-

phosphates in 3:1 concentrates at concentrations greater than 1 g. polyphosphate per 100 g. milk solids. Concentrates containing 0.13 g. or less polyphosphate per 100 g. milk (12.6% solids) had initial viscosities (viscosity measured before storage) comparable in magnitude to the viscosity of the control concentrate; concentrates containing 0.25 g. polyphosphate per 100 g. milk (12.6% solids) had a viscosity 15 times greater than that of the control.

A large number of experiments were carried out employing the laboratory techniques of Leviton and Pallansch for the preparation and study of HTST sterilized milk concentrates (2). These studies showed that the storage life was significantly increased in the presence of added polyphosphate, that the increase varied with additive concentration and that the rate of increase was more pronounced at the lower concentration levels (5). Employed at a concentration level of approximately 0.05% based on the original milk, the effect of polyphosphates with an average chain length greater than 4, was to increase storage life at 30°C of 3:1 concentrates from 2–3 weeks to many months. Likewise, the storage life of 2:1 concentrates was raised from 3–4 months to more than 9 months. The effectiveness of the polyphosphates increased with increasing chain length, and the cyclic condensed phosphates were found to be more effective than the corresponding chain polyphosphates.

Frozen Milk Concentrates

The concentrate containing slightly more than 35% solids was prepared from pasteurized milk homogenized at 2500–500 p.s.i. at the pasteurizing temperature. Final concentration adjustment to 35% solids was made with water or additive solution. Two additive concentrations were employed. Each batch was divided in two parts. To one part 10 g. of fine lactose crystals were dispersed in 10 lbs. of cold concentrate just prior to the filling of the cans. The control was not seeded. Samples were frozen at ÷17.8°C. Sediment and viscosity were measured periodically. Data are recorded in Table 2. Added polyphosphate effected a significant prolongation in storage life even in seeded samples. In agreement with the results of other investigators, it was found that lactose crystallization was a concomitant of instability and when crystallization was initiated by seeding storage life was shortened (7). The effect of additive in prolonging storage life was concentration dependent.

The orthophosphates destabilized frozen milk concentrates. Substitution of polyphates for 20% of the orthophosphates increased storage life slightly. In one series of experiments (data not presented) storage lives of 20, 28, 28 and 129 days were respectively for the following 31.5% unseeded concentrates: (a) concentrate containing 0.2% orthophosphate buffer salts based on 12.6% milk; (b) concentrate as in (a) in which 20% of the orthophosphate was replaced by pyrophosphate; (c) concentrate as in (a) in which 20% of the orthophosphate was replaced by tetraphosphate, and (d) concentrate containing approximately 0.2% tetraphosphate.

TABLE 2

Effect of Addition of Sodium Tetrapolyphosphate on Thickening and Gelation of Frozen Concentrated Milk

Storage Time	No Additive				.075% Tetrapolyphosphate				.15% Tetrapolyphosphate			
	Not Seeded		Seeded		Not Seeded		Seeded		Not Seeded		Seeded	
	Visc.	Sed.	Visc.	Sed.	Visc.	Sed.	Visc.	Sed.	Visc.	Sed.	Visc.	Sed.
days	cp	%	cp	%	cp	%	cp	%	cp	%	cp	%
0	14	0	14	0	18	0	18	0	26	0	26	0
22	15	3	244	29	20	0	47	1	34	0	60	0
53	gel	33	gel	33	345	25	gel	25	46	0	105	0
87	—	—	—	—	—	—	—	—	54	0	120	0

The salt was added to concentrate of 35% total solids before freezing at ÷17.8°C for 24 hrs. and storage at ÷12.2°C.
Additive concentration expressed as per cent of weight of 12.6%TS milk used.
Sediments (Sed.) determined on reconstituted milks containing 12.6% solids.
Viscosity (Visc.) measured at 30°C on concentrate held at 30°C for 1 hr.

Seeding effected a significant shortening of storage life in all but the polyphosphate containing concentrate.

Sweetened Condensed Milk

Milk forewarmed at 93°C for 15 seconds was concentrated to 32% total solids and to it was added the required amount of sucrose dissolved in an equal weight of raw milk. The solution of sucrose in milk also was heated at 95°C for 15 seconds. Concentration was continued beyond the total solids content desired and the sweetened condensed milk then was standardized with water or a solution containing sodium tetrapolyphosphate. On being cooled to 30°C, the concentrates were seeded with lactose, stirred slowly for one hour and stored in sealed cans at

TABLE 3

Effect of Addition of Sodium Tetrapolyphosphate on Thickening of Sweetened Condensed Milk

Storage Time	*Viscosity at 26.8°C*		
	No Additive	*.03% Tetrapolyphosphate*	*0.06% Tetrapolyphosphate*
1	2,000	2,160	2,360
8	2,000	2,120	11,520
30	2,360	1,400	26,200
90	13,200	3,000	37,400
115	14,360	6,880	47,200

Composition of sweetened condensed milk: Fat–8.5%, S.N.F.–20%, sugar–44%.
Storage temperature: 26.7°C.
Additive concentration expressed as per cent of weight of fluid milk used.
Data developed by R. W. Bell, Dairy Products Laboratory.

27°. Viscosity measurements were made periodically. Typical data recorded in Table 3, show that with the use of an optimum concentration of polyphosphate a marked retardation in age thickening of the sweetened condensed milk was brought about.

The employment of a concentration level greater than the optimum promoted rather than delayed thickening.

DISCUSSION

The action of the polyphosphates in retarding age thickening and gelation in the three low heat concentrates supports the hypothesis of a common coagulation mechanism. The results have important practical implications especially with respect to gelation in sterilized concentrates. The seriousness of the defect in such concentrates has delayed their market development despite their considerable flavor advantage.

Limiting the effectiveness of the polyphosphates is their slow conversion to orthophosphates. Inasmuch as the orthophosphates accelerate the gelation rate, the net result of hydrolysis is magnified to the extent that the orthophosphates are

formed. The greater the chain length the slower would be the hydrolysis and the less noticeable would be the contribution to destabilization of increasing orthophosphate concentration. The cyclic phosphates, because they resist hydrolysis to the chain polyphosphates, have the advantage, when used in milk, of possessing a greater over-all stability compared with the corresponding linear compounds.

Although the temptation to associate the behavior of the polyphosphates with their well-known calcium complexing ability is great, there are a number of cogent considerations which militate against the acceptance of this view. Thus added Ca++ retards gelation somewhat, and added orthophosphates accelerate it. Finally the cyclic condensed phosphates with no initial calcium complexing ability are more effective than the corresponding calium complexing linear polyphosphates.

The studies of Doan and Warren (3), and those of Wallgren (6) on frozen milk concentrates, although appearing to substantiate and support the findings reported in this paper, must be treated with thoughtful consideration. Protein instability in frozen milk is related to lactose crystallization during storage and therefore lactose crystallization must be controlled in studies on additives. Whether the polyphosphates are exerting a true anticoagulant effect can be decided only if their effect on lactose crystallization is not significant. In the experiments of Wallgren extremely viscous products were stored, and the viscosity of the additive containing product was of an order of magnitude higher than that of the control concentrate. Furthermore, the experimental conditions were such that lactose crystallization was restrained rather than expedited (8). Under these conditions, it would be difficult to decide whether the polyphosphates were functioning as anticoagulants. Much the same problem arises in interpreting the results of Doan and Warren.

Rather drastic conditions of reconstitution were employed by Doan and Warren involving the use of water at 82.2°C for thawing and reconstituting. Wallgren thawed his samples by placing the cans in one liter of water at 122°F for 30 minutes. The polyphosphates are capable of exerting a profound peptizing action on insoluble proteins. Thus if the conditions of reconstitution are too drastic, insolubilization of proteins during storage, if it occurred, might be masked by the peptizing effect of the polyphosphates.

Before concluding, it is important to refer to the recent work of Hoff *et al.*, on irradiation (9). Sterilization of milk concentrates with ionizing radiation was observed to result in protein destabilization. The irradiated milk coagulated instanteously at 90°C, and moreover, gelled quite rapidly at 37°C. The marked heat instability at 90°C shown by irradiated milk is not shared by HTST sterilized milk. This may be considered as evidence that the micellar structure and/or the micellar environment differ in the two types of sterile products and that consequently the mechanism of gelation in each is not necessarily related. However, since the polyphosphates, but not the orthophosphates, have been shown in our paper to stabilize HTST milk against gelation and similar effects in irradiated milk have been observed by Hoff *et al.*, it can be concluded that gelation in both

types of milk is governed by a common mechanism. This is supported by certain experimental data which will be considered in another paper.

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Effect of Phosphate Salts on the Thickening and Gelation of Some Concentrated Milks

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SUMMARY

The action of added tetrapolyphosphate glass in effectively retarding age thickening and gelation in the three low heat milk products – high temperature-short time sterilized, frozen and sweetened concentrate – indicate that the phenomenon of gelation is governed by a common mechanism. Concentrates containing 0.05 to 0.15% additive based on the fluid milk had storage lives up to six times that of additive-free concentrates. Small additions of polyphosphates provide a promising practical means for prolonging storage life.

Section V:2

L'effet des sels de phosphate sur l'épaissement et la congélation des laits concentrés

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RESUME

L'action d'ajouter du tétrapolyphosphate de verre pour retarder effectivement l'épaississement et la congélation des trois produits laitiers chauffés à basse température — les concentrés stérilisés à haute température pendant une courte durée, congélés et sucrés — indique que le phénomène de la congélation est contrôlé par un mécanisme commun. Les concentrés contenant de 0,05 à 0,15% d'additif basé sur le lait liquide possédaient une vie d'emmagasinage six fois plus longue que celle des concentrés sans additif. De petites additions de polyphosphate représentent une méthode pratique et intéressante pour prolonger la vie d'emmagasinage.

Die Wirkung phosphorsaurer Salze auf das Nachdicken und Gelieren einiger Arten von konzentrierter Milch

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ZUSAMMENFASSUNG

Die Wirkung eines Zusatzes von glasigem Natriumtetraphosphat zwecks Verhütung bzw. Verzögerung des Nachdickens und Gelierens der drei niedrig erhitzten Milchprodukte — hochtemperaturkurzzeitsterilisierte, gefrorene und gesüsste Konzentrate — deutet darauf hin, dass das Auftreten des Gelierens durch einen gemeinsamen Mechanismus gesteuert wird. Konzentrate, welche einen Zusatz von 0.05 bis 0.15%, bezogen auf flüssige Milch, erhielten, wiesen eine sechs mal so hohe Lagerfähigkeit auf wie zusatzfreie Konzentrate. Ein geringer Zusatz von Polyphosphaten bietet ein vielversprechendes praktisches Mittel, die Lagerfähigkeit zu erhöhen.

Section V:2

Virkningen af fosfatsalte på fortykkelsen og geleringen af forskellige typer koncentreret mælk

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SAMMENDRAG

Funktionen af tilsat amorft tetrapolyfosfat i deres evne til effektivt at hæmme fortykkelsen og geleringen af tre typer mælkeprodukter — høj-temperatur-korttidssteriliseret, frosset og sukkertilsat koncentrat — viser, at geleringsfænomenet er underkastet en fælles mekanisme.

Koncentrater, der indeholder 0,05—0,15% tilsætning baseret på den uinddampede mælk havde lagringstider, som var 6 gange større end koncentrater uden tilsætninger. Små tilsætninger af polyfosfater frembyder en praktisk måde til at forlænge lagringstiden.